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CATALYTIC CRACKING OF HYDROCARBONS

Filed Feb. 18, 1944

2 Sheets-Sheet 1

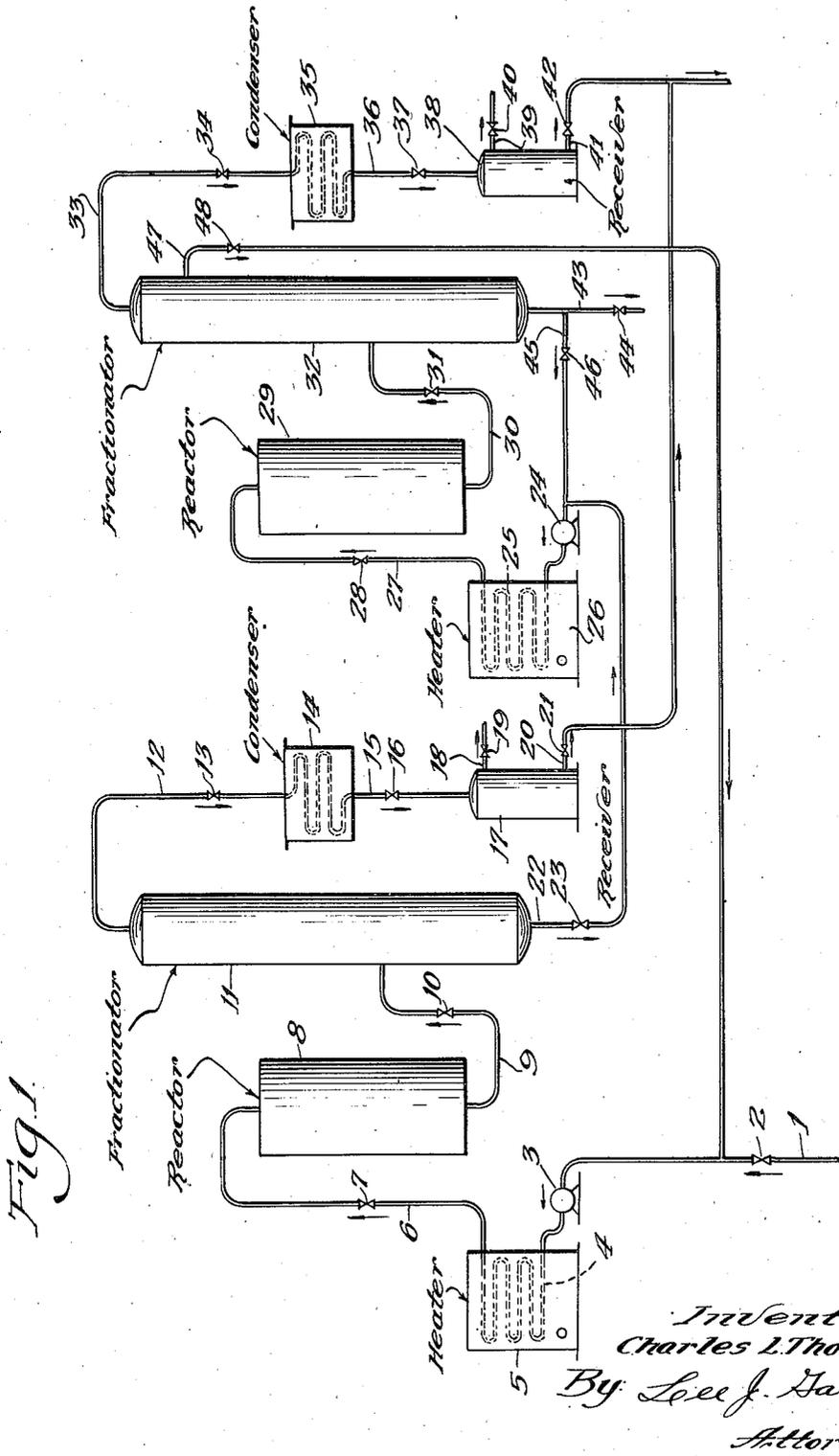


Fig. 1

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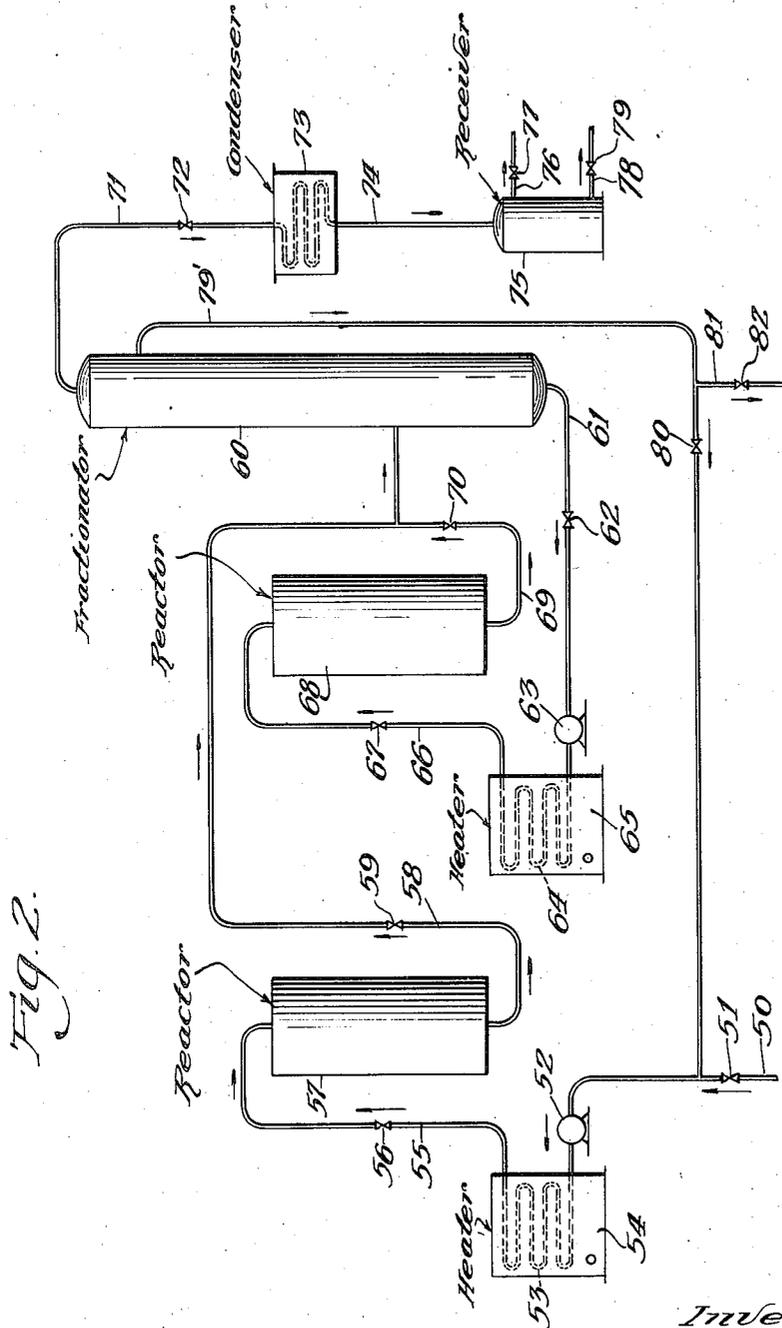


Fig. 2.

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UNITED STATES PATENT OFFICE

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CATALYTIC CRACKING OF HYDROCARBONS

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Application February 18, 1944, Serial No. 522,855

6 Claims. (Cl. 196—49)

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This application is a continuation-in-part of my co-pending application Serial No. 296,067, filed September 22, 1939, now abandoned.

This invention relates to a process for converting hydrocarbon oil to motor fuel and more particularly to the production of a catalytically cracked gasoline suitable for use as an aviation base fuel.

It is desirable in aviation base fuels that they have a low content of olefinic hydrocarbons which tend to develop gum during extended periods of storage.

The present invention concerns a method of producing high yields of relatively saturated aviation base stock by means of catalytic conversion of hydrocarbon oils.

Broadly, the invention relates to a process for converting hydrocarbon oil into substantial yields of relatively high antiknock motor fuel having a high degree of susceptibility to lead tetraethyl which comprises contacting said hydrocarbon oil with a cracking catalyst in a primary cracking step at a temperature of 500–900° F. and at cracking conditions to effect moderate conversion and produce a relatively saturated gasoline, separating said gasoline, contacting the insufficiently converted oil from the primary step with a cracking catalyst in a secondary cracking step at a temperature of approximately 900–1200° F. and at cracking conditions to effect a high degree of conversion and produce a relatively olefin-free gasoline, and separating said last mentioned gasoline.

In a more specific embodiment the present invention comprises a process for converting hydrocarbon oil into substantial yields of relatively high antiknock fuel in which said hydrocarbon oil is contacted with a cracking catalyst in a primary cracking step at a temperature of 500–900° F. and at cracking conditions to effect moderate conversion and produce a relatively saturated gasoline, separating said gasoline, contacting the insufficiently converted oil from the primary step with a cracking catalyst in a secondary cracking step at a temperature of approximately 900–1200° F. and at cracking conditions adequate to effect a high degree of conversion and produce a relatively saturated highly aromatic gasoline and an intermediate highly aromatic fraction, separating said last mentioned gasoline and blending it with said first mentioned gasoline, and returning said highly aromatic intermediate fraction to the primary cracking step to undergo conversion with said hydrocarbon oil.

In the cracking of hydrocarbon oils, conversion has been defined by several different means. For

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example, conversion may be defined as the quantity of a particular boiling range gasoline fraction produced as compared to the original charge. It also may be defined as the percentage by weight of the charge which is converted to gasoline plus gas plus coke. I prefer the latter definition for conversion and hereinafter in this specification and claims, unless otherwise noted, conversion is intended to have this preferred meaning.

It has been found when treating a virgin cracking stock that low temperatures and moderate conversions result in the most economical yield of relatively saturated high antiknock motor fuels suitable for aviation base stock. The degree of conversion which is attained in catalytic cracking processes is dependent upon several factors including the particular catalyst employed, the charging rate of the material to be cracked, the ratio of regenerated catalyst to the quantity of oil treated, and the temperature of operation. In general, conversion increases with increases in temperature, and increases in the ratio of catalyst to oil and decreases with increases in the charging rate of the material to be cracked. Of the several operating variables which must be considered in catalytic cracking those which have the greatest effect on product quality are conversion and the character of the hydrocarbon oil being treated. For example, with increases in conversion the saturation of the product increases as well as the aromatic content. As the character of the charging stock is changed from paraffinic to naphthenic the saturation of the product increases and the aromatic content of the product increases.

In relating gasoline yield to conversion, it has been found that the gasoline yield increases with conversion to a maximum and then declines as the conversion increases further. The point of maximum gasoline yield decreases as the temperature increases. In the process herein disclosed the virgin cracking stock is treated at a cracking temperature under about 900° F. and at a moderate conversion corresponding to a point in the conversion against gasoline yield curve which is on the low conversion side of the maximum. By operating at these conditions, the highest yield of saturated product is obtainable with the least degradation of the cracking stock. The particular conversion to be employed will vary with the cracking stock to be treated but in general with virgin stocks will be from about 25% to about 60% by weight of the charge.

In the second stage of my process I intend treating the more refractory insufficiently converted hydrocarbon oil from the first stage to

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produce a relatively saturated product containing a high proportion of aromatic hydrocarbons. In this step of the process I intend operating to obtain a conversion which corresponds to a point on the conversion against gasoline yield curve which is on the high conversion side of the maximum gasoline yield point which will, with refractory stocks, be not less than a conversion of about 60% by weight of the charge. It has been found that when operating at the high conversions contemplated for use in this invention, a saturated gasoline product containing a high percentage of aromatic hydrocarbons is produced. However, in order to obtain the high conversion and the aromatic gasoline necessary to satisfactorily accomplish my invention, it is necessary when using the refractory stock from the first step to operate at temperatures above about 900° F.

In the more specific embodiment of the invention wherein the intermediate aromatic fraction (300–450° F. boiling range) produced in the high temperature step is to be converted to gasoline boiling range aromatics, it has been found that more selective dealkylation of the poly alkylated aromatics present in this material may be obtained when the temperature conditions of conversion are below about 900° F. It is, therefore, one of the features of this invention to return this material to the low temperature step of the process in order to more selectively dealkylate the aromatics to produce alkylated aromatics which are more suitable for use in aviation gasoline.

Catalytic materials useful in the primary and secondary cracking steps of this process include any suitable cracking catalyst but are preferably of the synthetic precipitated silica-alumina, silica-zirconia, and silica-alumina-zirconia type. The catalyst may be employed in the form of pills, granules, or powder depending upon the particular apparatus in which is to be used. For example, in fixed or moving bed processes the pill or granular forms are in general more desirable, while in the so-called fluidized bed process finely divided catalyst in the form of powder or small granules or formed particles will give excellent results.

Although the present process is usually operated with a similar catalytic agent in both the primary and secondary cracking steps it is well within the scope of the invention to use a different catalytic mass in each step.

During the cracking reaction there is an accumulation of carbonaceous or hydrocarbonaceous material on the catalytic surface which reduces their activity. These materials are ordinarily removed by burning in an oxygen containing gas to reactivate the catalyst.

When employing a fixed bed process the catalytic mass is alternately contacted with reactant materials and with the oxygen containing gas with the necessary purging steps intermediate the other two periods of the process. When employing moving bed or fluidized bed processes, the catalyst is ordinarily transferred between the reaction zone wherein it is contacted with the reactant material and the regenerating zone wherein it is contacted with oxygen containing gas. The transportation of the catalyst between the two zones may be accomplished by various means including mechanical conveyors and elevators. In some cases the reactant materials and regenerating gas are used as transportation means for the catalyst.

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In order to make the invention more apparent and thoroughly understood reference is made to the accompanying diagrammatic drawing.

Figure 1 of the drawing illustrates one form of apparatus suitable for conducting the process of the invention. In this particular form separate fractionating columns are provided for the two cracking steps.

Figure 2 illustrates an alternative form of apparatus suitable for conducting the process of the invention in which a single fractionating column is employed for both cracking steps.

Referring now to Figure 1, the charging stock is supplied through line 1 and valve 2 by means of pump 3 to heating coil 4 located in heater 5. In the heating coil the charging material is heated to a temperature of from 500–900° F. and is then directed through line 6 and valve 7 into reactor 8. The apparatus illustrated is of the fixed bed type and only a single reactor is shown. However, in practice in order to obtain continuity of operation at least two reactors would be employed, in order that while one is being regenerated the other may be processing the reactant material.

The reaction products from the reactor are directed through line 9 and valve 10 into fractionator 11 wherein an overhead product having the desired end boiling point is separated from the insufficiently converted material. The overhead product is passed through line 12 and valve 13 into condenser 14 wherein the product is cooled and the resultant distillate is directed by means of line 15 and valve 16 into receiver 17. In receiver 17 the uncondensed gases are separated from the condensate and are removed from the system through line 18 and valve 19. The condensate is removed from the system through line 20 and valve 21.

The insufficiently converted material from the first step is removed from fractionator 11 through line 22 and valve 23 and directed by means of pump 24 into heating coil 25 disposed within heater 26. The oil passing through coil 25 is heated to a temperature of from about 900° F. to about 1200° F. and then directed by means of line 27 and valve 28 into reactor 29. Although only one reactor is shown in the drawing it is to be understood that in practice a plurality of such reactors would be employed. From reactor 29, the reaction products are directed by means of line 30 and valve 31 into fractionator 32. An overhead product having the desired end boiling point is removed by means of line 33 and valve 34 and directed into condenser 35. The cooled material from condenser 35 is then directed through line 36 and valve 37 into receiver 38. In receiver 38 the uncondensed gases are separated from the condensate and the former is removed from the system through line 39 and valve 40. The condensate is removed from the system through line 41 and valve 42 and commingled with the condensate produced in the first stage of the process to be directed to suitable equipment for stabilization and the like.

The insufficiently converted material is removed from fractionator 32 and withdrawn from the process through line 43 and valve 44, or when desired this material may be directed through line 45 and valve 46 to be commingled with material from the first stage of the process passing through line 22.

In some instances where it is desirable that the gasoline product be high in aromatic content an intermediate fraction boiling from about 300 to

450° F. is removed from fractionator 32 by means of line 47 and valve 48 to be commingled with the charging stock passing through line 1.

Referring now to Figure 2, charging stock for the process is introduced through line 50 controlled by valve 51 and discharged from pump 52 into heating coil 53 disposed within heater 54. The oil passing through coil 53 is heated to a temperature of from about 500-900° F. and then passed through line 55 and valve 56 into reactor 57. The reaction products from reactor 57 are passed through line 58 and valve 59 into fractionator 60. The insufficiently converted material removed from the bottom of fractionator 60 is passed through line 61, valve 62, and pump 63 into heating coil 64 disposed within heater 65. In heating coil 64 the oil is heated to a temperature of from about 900-1200° F. and then passed through line 66 and valve 67 into reactor 68. The resultant conversion products are removed from reactor 68 by means of line 69 and valve 70, commingled with the material passing through line 58 and thence directed into fractionator 60. The overhead product from fractionator 60 containing the desired end point gasoline is withdrawn through line 71 and valve 72 and passed into condenser 73. The cooled material from condenser 73 is then directed by line 74 into receiver 75. In receiver 75 the uncondensed gases are separated and removed from the process through line 76 and valve 77 and the resultant liquid condensate is removed from the system through line 78 and valve 79. An intermediate naphtha fraction high in aromatics is withdrawn from fractionator 60 by means of line 79' and valve 80 and commingled with the charging stock in line 50 or when desired this material may be withdrawn from the system through line 81 and valve 82.

In order to further illustrate the utility of the invention the following example is included. It is, however, not to be construed as a limitation of the invention.

A Mid-Continent gas oil having a gravity of 37.1° A. P. I. is passed into the first stage reactor which is maintained at about 825° F. and slightly superatmospheric pressure. The charging material is passed through the catalyst bed at a weight hourly space velocity of 2 and the process period length is regulated to give a conversion of 40%. The resultant gasoline and gas are separated from the insufficiently converted material and the latter is then passed through a second stage reactor maintained at 950° F. and slightly superatmospheric pressure. The materials undergoing conversion are passed through the catalyst mass at a weight hourly space velocity of 1.8 and the process period length is regulated to give a conversion of 65%. The gasoline and gas are separated from the insufficiently converted material and the latter recycled through the second stage of the process. The gasoline and gas produced in each of the stages are mixed and the following is a tabulation of the yields obtained in the process:

Yield wt. percent of the charge	
300° F. E. P. depent, gaso.....	44.5
Carbon	9.3
C ₃ , C ₄ , C ₅ olefins.....	16.5
Isobutane	11.7
Isopentane	8.2
Normal C ₆ - and dry gas.....	9.8
Total	100.0

The above gasoline which contains 45% aromatics has a bromine number of 17 and has a 1-C rating with 4 cc. of tetraethyl lead of 96. The isopentane produced may be used to increase the vapor pressure of the gasoline and at the same time increase its antiknock rating. The higher olefins and isobutane may be converted into alkylates and polymers which have a high aviation gasoline blending value.

The 1-C method is described in A. S. T. M. 614-41T.

I claim as my invention:

1. A process for the production of substantially saturated gasoline which comprises introducing a hydrocarbon oil into a primary cracking zone and therein contacting said oil with a cracking catalyst at a cracking and dealkylating temperature below about 900° F., correlating the charge rate of said hydrocarbon oil to said primary cracking zone and the ratio of catalyst to oil in said zone with said cracking temperature to effect a conversion of said hydrocarbon oil of not more than 60% and to produce a substantially saturated gasoline, separating from the resultant products said substantially saturated gasoline and a higher boiling insufficiently converted hydrocarbon oil, introducing the latter into a secondary cracking zone and therein contacting said insufficiently converted hydrocarbon oil with a cracking catalyst at a cracking temperature above about 900° F., correlating the charge rate of hydrocarbon oil to said secondary cracking zone and the ratio of catalyst to oil therein with said last named cracking temperature to effect a conversion of said insufficiently converted hydrocarbon oil of at least 60% and to produce a substantially saturated gasoline, separating from the reaction products of said secondary cracking zone said last named gasoline and a polyalkylaromatic fraction boiling within the range of from about 300° F. to about 450° F., and recycling said polyalkylaromatic fraction to said primary cracking zone to selectively dealkylate the same at said dealkylating temperature.
2. The process of claim 1 wherein the catalyst employed in each of said cracking zones consists of a composite of silica and alumina.
3. The process of claim 1 wherein the catalyst employed in each of said cracking zones consists of a composite of silica and zirconia.
4. The process of claim 1 wherein the catalyst employed in each of said cracking zones consists of a composite of silica, alumina, and zirconia.
5. The process of claim 1 further characterized in that the conversion in said primary cracking zone is from about 25% to about 60%.
6. A process for the production of substantially saturated gasoline which comprises introducing a hydrocarbon oil into a primary cracking zone and therein contacting said oil with a cracking catalyst at a cracking and dealkylating temperature below about 900° F., correlating the charge rate of said hydrocarbon oil to said primary cracking zone and the ratio of catalyst to oil in said zone with said cracking temperature to effect a conversion of said hydrocarbon oil of not more than 60% and to produce a substantially saturated gasoline, introducing the resultant products into a fractionating zone and withdrawing therefrom insufficiently converted hydrocarbon oil, introducing the latter into a secondary cracking zone and therein contacting said insufficiently converted hydrocarbon oil with a cracking catalyst at a cracking temperature above about 900° F., correlating the charge rate of hydrocarbon oil to

said secondary cracking zone and the ratio of catalyst to oil therein with said last named cracking temperature to effect a conversion of said insufficiently converted hydrocarbon oil of at least 60% and to produce a substantially saturated gasoline, introducing the reaction products from said secondary cracking zone into said fractionating zone, separating in said fractionating zone a substantially saturated gasoline fraction and a polyalkylaromatic fraction boiling within the range of from about 300° F. to about 450° F., and recycling said polyalkylaromatic fraction to said primary cracking zone to selectively dealkylate the same at said dealkylating temperature.

CHARLES L. THOMAS.

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